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(HBCU) - Required Equipment for Photo-switchable Donor-Acceptor (D-A) Dyad Interfacial Self-Assembled Monolayers for Organic Photovoltaic Cells

LUIS ECHEGOYEN

UNIVERSITY OF TEXAS AT EL PASO

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Final Report

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14. ABSTRACT Seven major instruments were purchased: 1) A DXR Smart Raman spectrometer, 2) A Bruker Tensor 27 FT Infrared Spectrometer, 3) An Alpha-Step D-120 Profilometer from KLA Tencor Corp., 4) A Rame-Hart model 250 Goniometer/Tensiometer, 5) an Agilent Diffuse Reflectance Accessory, 6) a Jelight Co. UVO cleaner, and 7) a Laurell Technologies Spin Coater. These instruments were used to characterize a variety of photoswitchable Donor-Acceptor (DA) dyads that were designed, synthesized, and evaluated as Interfacial Layers (ILs) in Organic Photovoltaic (OPV) devices and in Dye-Sensitized Solar Cells (DSSCs). Proof of the original proposal concept, photoswitched ILs, was unambiguously established.					
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Final Report

Luis Echegoyen - FA9550-12-1-0468

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1. Publications Acknowledging Grant

- a) Alexis Tigreros, Vivek Dhas, Alejandro Ortiz, Braulio Insuasty, Nazario Martín and Luis Echegoyen, "Influence of acetylene-linked π -spacers on triphenylamine-fluorene dye sensitized solar cells performance," *Solar Energy Mater. And Solar Cells*, 121, 61-68, 2014.
- b) Mahsa Hosseini, Danisha M. Rivera-Nazario, Ping Peng, and Luis Echegoyen, "Self-Assembled Monolayers of C₆₀-Triphenylamine Dyads as Photo-Switched Interfacial Layers for Potential Application in Photovoltaic Cells," *ACS Applied Materials & Interfaces*, 2014, submitted.
- c) Danny Arteaga, Robert Cotta, Alejandro Ortiz, Braulio Insuasty, Nazario Martín and Luis Echegoyen, "New Zn(II)-porphyrin dyes with several electron acceptor groups linked by vinylfluorene and vinyl-thiophene spacers for dye-sensitized solar cells," *Chem. Eur. J.*, 2014, submitted.

2. Introduction

The design and syntheses of novel fullerene-based compounds for potential applications in organic solar cells is the main topic of this report. Each of the following sections consists of a brief introduction to the topic and discussion of results. The experimental section consists of instrumentation, methods, syntheses and characterization data for relevant compounds.

3. Organic Photovoltaics (OPV) and Interfacial Layers

A typical organic photovoltaic device is represented diagrammatically in Figure 1. Interfacial layers (electron-blocking/hole-transporting, EBL/HTL, or hole-blocking/electron-conducting, HBL/ECL) between the electrodes and the photoactive layer have been incorporated to improve charge collection and ohmic contacts.¹⁻³ The most studied interfacial layer between the anode and the photoactive layer is the negatively charged polymer poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) that possesses good hole transporting ability. However, inhomogeneities at the surface of the electrode after deposition of the polymer lower the stability and performance of the OPV devices. Self-assembled monolayers (SAMs) have been used as interfacial layers and they have improved ohmic contacts and charge collection.^{4,5}

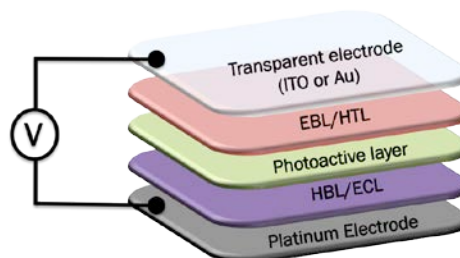


Figure 1. Cell configuration of organic photovoltaics.

Theoretically, if PEDOT:PSS is substituted with a neutral self-assembled monolayer that can produce a charge-separated state upon exposure to light, device efficiencies should increase by cell polarization (Figure 2). Thus, donor-acceptor (D-A) fullerene dyads were proposed as potential photo-switched polarizing layers for enhanced efficiencies of solar cell devices. Proper collection of charges at the electrodes is an important parameter in organic solar cells. Interfacial layers between the electrodes and the photoactive layer have been incorporated to improve charge collection and ohmic contacts.¹⁻³ The most studied interfacial layer between the anode and the photoactive layer is the negatively charged polymer poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) that possesses good hole transporting ability. However, inhomogeneities at the surface of the electrode after deposition of the polymer lower the stability and performance of the OPV devices. Self-assembled monolayers (SAMs) have been used as interfacial layers and they have improve ohmic contacts and charge collection.⁴⁻⁵ In principle, if PEDOT:PSS is replaced by a neutral self-assembled monolayer that can produce a charge-separated state upon exposure to light, device efficiencies should increase by cell polarization (Figure 2). Therefore, we proposed donor-acceptor fullerene-based dyads as potential photo-switched polarizing layers for enhanced efficiencies of solar cell devices.

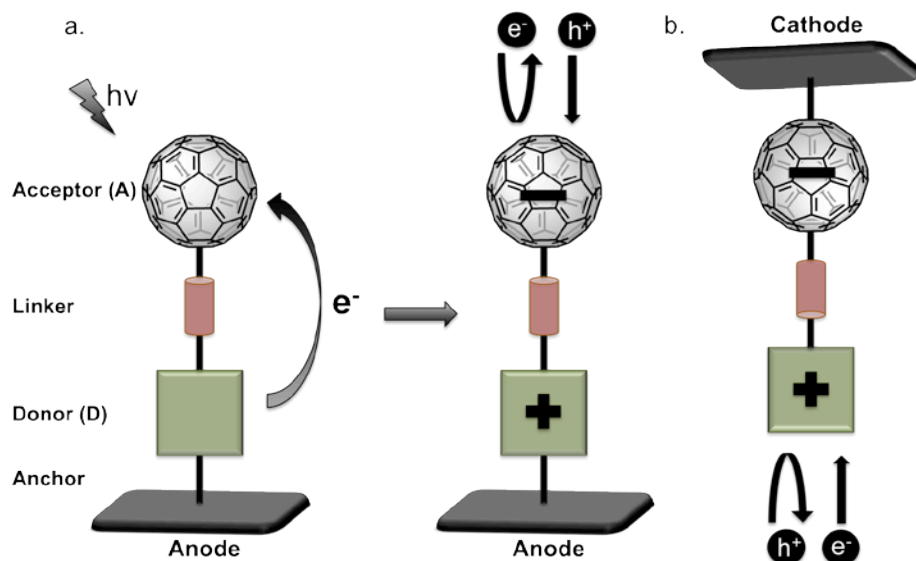


Figure 2. Overall Concept. Illustration of an (a) electron transfer from donor (D) to acceptor (A) upon light irradiation and its corresponding charge-separated state D^+-A^- leading to an electron blocking/hole transporting layer (EB/HT). (b) Inverted orientation of charge-separated state (HB/ET).

organic solar cells. Interfacial layers between the electrodes and the photoactive layer have been incorporated to improve charge collection and ohmic contacts.¹⁻³ The most studied interfacial layer between the anode and the photoactive layer is the negatively charged polymer poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) that possesses good hole transporting ability. However, inhomogeneities at the surface of the electrode after deposition of the polymer lower the stability and performance of the OPV devices. Self-assembled monolayers (SAMs) have been used as interfacial layers and they have improve ohmic contacts and charge collection.⁴⁻⁵ In principle, if PEDOT:PSS is replaced by a neutral self-assembled monolayer that can produce a charge-separated state upon exposure to light, device efficiencies should increase by cell polarization (Figure 2). Therefore, we proposed donor-acceptor fullerene-based dyads as potential photo-switched polarizing layers for enhanced efficiencies of solar cell devices.

C₆₀-TPA dyads as photo-switched HB/ET interfacial layers in organic solar cells: Towards enhanced efficient OPV devices

Figure 3 shows the compounds we prepared to assemble on gold (Au) surfaces. Results of TPA-C₆₀ dyads (**1** and **2**) self-assembled on Au electrodes demonstrated that charge-separated states are produced upon exposure to light. Electrochemical impedance spectroscopy was used to study the

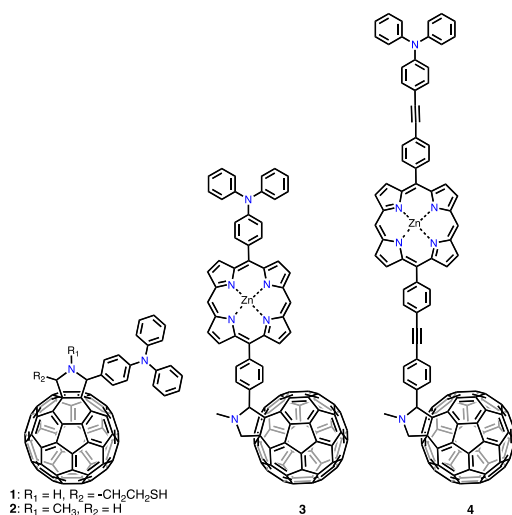


Figure 3. Triphenylamine- fullerene-based dyads to be self-assembled on Au surfaces.

photo-switched properties and to demonstrate the generation of charges at the surface of the modified electrodes. Two charged probes, $\text{Ru}(\text{NH}_3)_6^{2+/3+}$ and $\text{Fe}(\text{CN})_6^{3-/4-}$, were used to study the resistance to charge transfer across these photo-switched layers. Nyquist plots of the responses of these monolayers in the dark exhibit charge transfer resistances for both probes due to the presence of the monolayer (Figures 4a and 4b). After exposure to UV light, electron transfer from the excited donor to the acceptor generates a positively charged barrier at the surface of the electrode. After intramolecular electron transfer takes place, the resistance to charge transfer increases for the positively charged probe ($\text{Ru}(\text{NH}_3)_6^{2+/3+}$) and decreases for the negatively charged probe ($\text{Fe}(\text{CN})_6^{3-/4-}$), because of repulsion and attraction

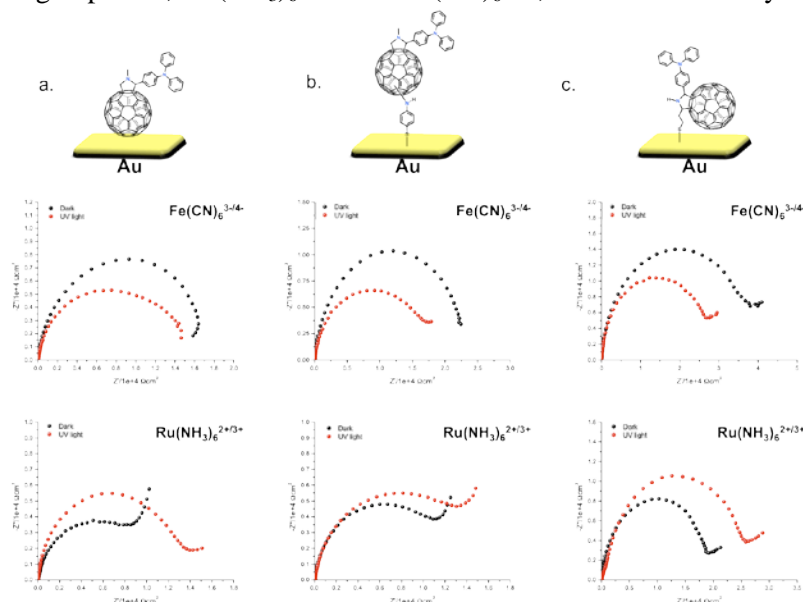


Figure 4a. Nyquist plots for self-assembled monolayers of **1** and **2**.

of charges, respectively. This desired trend was observed for all of the monolayers investigated. These results indicate that it is possible to polarize a cell by constructing a hole blocking/electron

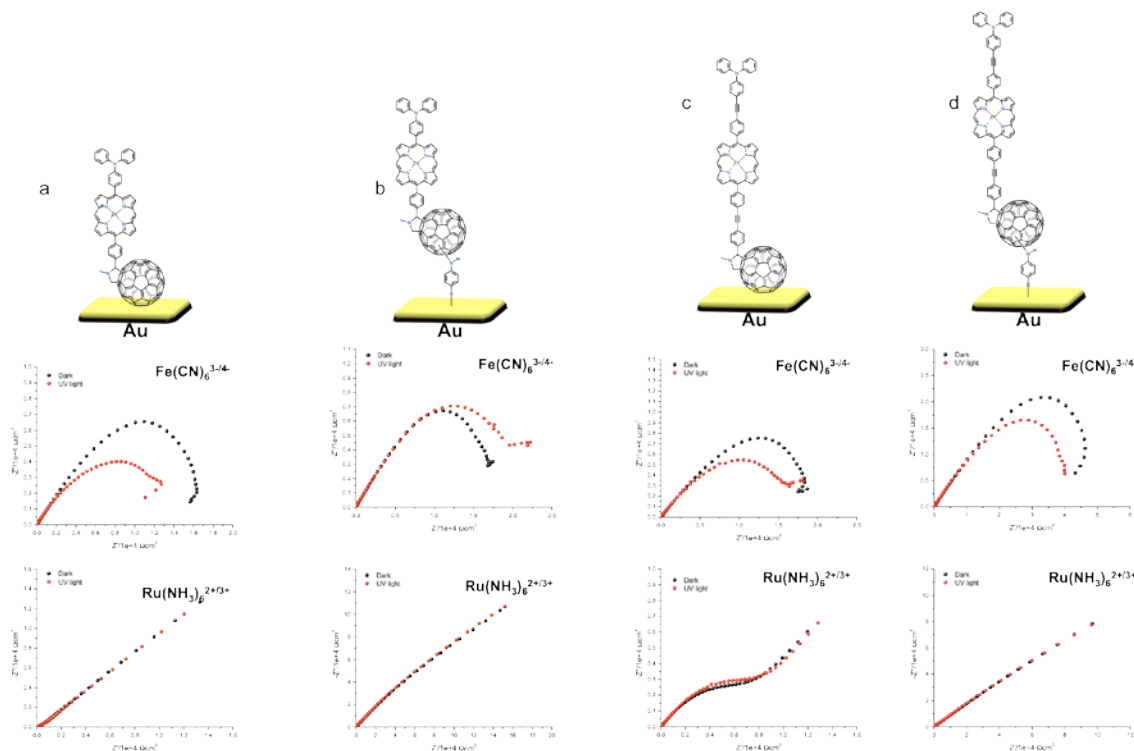


Figure 4b. Nyquist plots of self-assembled monolayers of **3** and **4**.

transporting layer and vice versa for a cathode/A-D/interface and anode/D-A/interface junctions, respectively. These results are submitted for publication, see reference 1b above, and conclusively and unambiguously demonstrate the proof of concept behind the original application.

C₆₀-Porphyrin dyads as EB/HT interfacial layers in organic solar cells: Towards enhanced efficient OPV devices

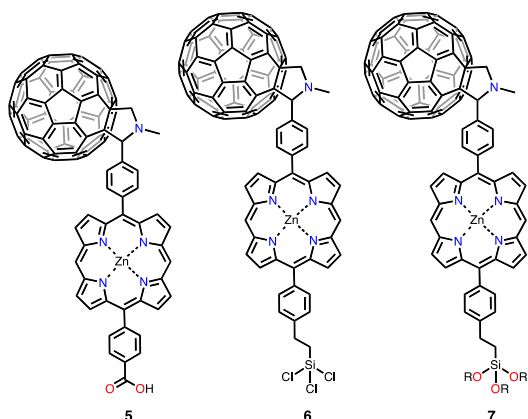


Figure 5. Potential porphyrin-based fullerene dyads to be used as interfacial layers on ITO electrodes.

Since $-\text{CO}_2\text{H}$ and $-\text{SiCl}_3$ ($-\text{Si}(\text{OR})_3$) as well attach strongly to ITO surfaces via strong adsorption and covalent bonding with the surface hydroxyl groups, respectively, we decided to prepare compounds **5-7** to attach as SAMs, see Figure 5. Difficulties and unexpected problems during the preparation of these compounds were encountered, so **6** and **7** were abandoned and we focused our attention in the preparation of dyad **5** that contains a functional group that can be adsorbed at the surface of the ITO (Figure 6a), and it can also react with terminal $-\text{NH}_2$ monolayers on ITO, as shown in Figure 6b. The successful synthesis of **5** was achieved and its self-assembled monolayer prepared on ITO

substrates. Effective immobilization of **5** on ITO was confirmed by solid-state UV-vis experiments. However, electrochemical impedance spectroscopy did not show high resistances even in the dark, meaning that the monolayers are not densely packed and pinholes are present at the modified electrode. If bare electrode sites are exposed to the spin coated photoactive layer over the ITO monolayer, the effectiveness of this monolayer will be difficult to study. We need to assure that a densely packed and organized self-assembled monolayer is formed. Monolayer treatment with alkyl terminated $-\text{NH}_2$ could be an efficient approach to a densely packed interfacial layer (Figure 6b). Synthesis of these compounds is underway.

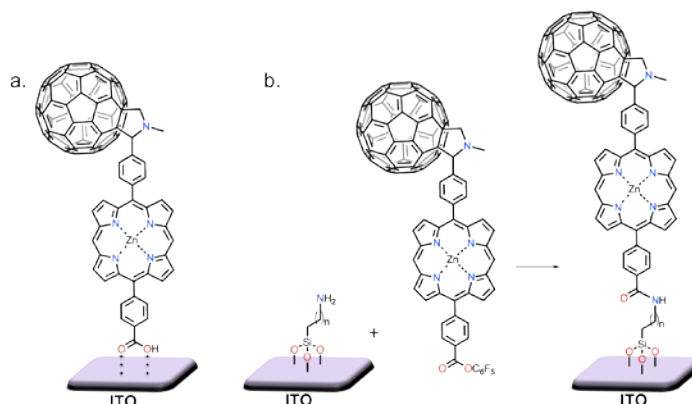


Figure 6. Self-assembled monolayers of **5** on ITO and possible interfacial reaction as an alternative anchoring.

4. Experimental Section

Instrumentation

^1H and ^{13}C NMR spectra were recorded on a JEOL ECA 600 NMR spectrometer at room temperature using CDCl_3 or $\text{THF-}d_8$ as solvent. UV-vis spectra were collected at room temperature using a Varian UV-Vis-NIR Cary 5000 spectrophotometer. Mass spectra were obtained using a Bruker microFlex MALDI-TOF spectrometer on reflector positive mode using 1,8,9-trihydroxyanthracene as the matrix. Electrochemical experiments were performed with a

CHI-660A electrochemical workstation. Impedance measurements were performed in a 0.1 M NaPF₆ solution containing equal concentrations of Ru(NH₃)₆^{2+/3+} and Fe(CN)₆^{3-/4-} (~1 mM). The frequency range used was 10⁴ Hz to 0.1 Hz with AC amplitude of 5 mV. Contact angle of water were measured using a Ramé-Hart model 250 goniometer using pure deionized water at room temperature. A total of ten static measurements were analyzed and averaged for each self-assembled monolayer.

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